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The Potential for Composting Energetic Material Production Wastes

by

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U.S. Army installations that manufacture munitions generate large quantities of energetic material (EM) and solid waste contaminated with energetic material (energetic material-contaminated waste, or EMCW). Disposal of EM and EMCW by open burning or open detonation (OB/OD) has been the practice for many years, but increasingly stringent environmental regulations are curtailing OB/OD operations. Incineration is not extensively used because of the difficulty in siting needed facilities and the negative public perception often associated with incinerators. Other alternatives include controlled incineration, wet air oxidation, super critical water oxidation, and composting.

Although composting has been used in some instances for explosive-contaminated soils, it has not been examined for use with munitions production wastes. A literature search showed that many explosives are biodegradable and that some explosive-contaminated soils can also be treated by composting. A potential exists to treat munition production wastes by composting or other biological treatment processes. This study concluded that further investigation is needed to determine and test: (1) the energetic compounds that can be biodegraded, and (2) the conditions under which biological treatment processes can occur.



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Although composting has been used in some instances for explosive-contaminated soils, it has not been examined for use with munitions production wastes. A literature search showed that many explosives are biodegradable and that some explosive-contaminated soils can also be treated by composting. A potential exists to treat munition production wastes by composting or other biological treatment processes. This study concluded that further investigation is needed to determine and test: (1) the energetic compounds that can be biodegraded, and (2) the conditions under which biological treatment processes can occur.

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Foreword

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1 Introduction

Background

U.S. Army installations that manufacture munitions generate large quantities of energetic material (EM) and solid waste contaminated with energetic material (energetic material-contaminated waste, or EMCW). EM includes a wide assortment of explosives, propellants, and pyrotechnics. EMCW may include wood, paper, cloth, and solvents. Disposal of EM and EMCW by open burning (OB) or open detonation (OD) has been the practice for many years and is considered a "first generation" technology. Increasingly stringent environmental regulations are curtailing OB/OD operations and threaten to interrupt munitions production unless alternative methods of disposal are found. Incineration, considered a second generation technology, is not extensively used because of the difficulty in siting needed facilities and the negative public perception often associated with incinerators. Third generation alternatives under consideration include controlled incineration, wet air oxidation, super critical water oxidation, and composting. Although composting has been used in some instances for explosives-contaminated soils, it has not been examined for use with munitions production wastes. This report evaluates the potential for composting EM and EMCW based on previous laboratory and field studies.

Objectives

The objectives of this study were to determine if a potential exists for composting energetic material production wastes and to identify areas requiring further research to develop and implement this third generation technology.

Approach

A literature review was conducted of laboratory and field studies involving the biodegradation of energetic compounds. This information was analyzed, the potential for composting munition production wastes was evaluated, and areas requiring further study or consideration were identified.

Mode of Technology Transfer

It is anticipated that the information derived from this investigation will form the basis for further research to develop and implement the composting of energetic material waste.

2 Literature Review

Generation of Energetic Material Production Wastes

U.S. Army installations that manufacture explosives, propellants, and pyrotechnics generate waste EM and EMCW (collectively referred to as energetic material production wastes). A survey conducted by the U.S. Army Construction Engineering Research Laboratories (USACERL) estimates that 7,654 tons of munitions production wastes are generated each year at U.S. Army Materiel Command (AMC) facilities (Table 1).^{*} Waste EM is a combination of explosives, propellants, and pyrotechnics. EMCW may include wood, cloth, plastics, paper, and solvents, which may present a potential fire or explosive hazard.

Historically, the most frequently used method of disposal for munitions production wastes has been open burning or open detonation (OB/OD). OB/OD operations are

common at most U.S. Army installations that either manufacture, or load, assemble, and pack (LAP) munitions. OB/OD operations are being more stringently regulated by the environmental community because the process generates uncontrolled air emissions and has a potential for contaminating soil and ground water. Currently, the use of OB/OD requires a Resource Conservation and Recovery Act (RCRA) subpart X permit, which is granted case by case. Efforts to find alternative disposal methods for munitions production wastes have been under way for many years. Incineration is evolving as a second generation disposal technology, but is considered an uneconomical solution. Other alternatives are needed to minimize costs and ensure compliance with current and projected future environmental regulations.

Table 1. Waste energetic material and solid waste contaminated with energetic material produced (tons/year) at Army installations from 1988 to 1992.

Installations	EM	EMCW
Radford AAP	990	3,700
Redstone ARS	170	50
Lonestar AAP	160	140
Holston AAP	110	1,200
Crane AAP	93	44
McAlester AAP	30	19
Iowa AAP	24	422
Milan AAP	13	480
Lake City AAP	9	0
Totals	1,599	6,055
Grand Total	7,654	

^{*} 1 ton = 907.18 kg.

Biodegradation of Energetic Compounds

Biological processes are being used with increasing frequency to dispose of a variety of wastes and to remediate environments contaminated with toxic chemicals. Biological processes typically have lower costs than conventional treatment technologies, are better accepted by the general public, and can often reduce the waste material to the innocuous substances CO_2 and H_2O , or CO_2 and CH_4 . However, waste material must be susceptible to biodegradation before a biologically based process can be applied. Relatively little is known regarding the biodegradation of energetic compounds (Gorontzy et al. 1994). Although laboratory studies indicate that many energetic compounds can be biodegraded, little is known about the environmental conditions and physiological factors controlling their biodegradation.

Perhaps the most studied energetic compound is trinitrotoluene (TNT). Many studies have established the biodegradation of TNT under aerobic conditions (Walker and Kaplan 1992; Gorontzy et al. 1994; Kaplan and Kaplan 1982; Kaplan 1992; Pennington et al. 1994). Isomers of diaminonitrotoluene and hydroxylamino intermediates are frequently reported as intermediates under aerobic conditions. The hydroxylamino intermediates can either couple with each other to form azoxy compounds, or conjugate with the available organic matter (Kaplan and Kaplan 1982), increasing their recalcitrance to further biodegradation. While TNT is generally reported to be resistant to mineralization under aerobic conditions (Kaplan and Kaplan 1982; Gorontzy et al. 1994), studies with fungi have observed the mineralization of TNT (Gorontzy et al. 1994). Some studies have shown the transformation of TNT in the absence of oxygen under nitrate- and sulfate-reducing and methanogenic conditions (Boopathy, Wilson, and Kulpa 1993). A sulfate-reducing bacterium was isolated that was capable of using TNT as the sole source of nitrogen and was capable of reducing TNT to triaminotoluene and even further transforming it to unknown products (Preuss, Fimpel, and Diekert 1993). Biodegradation of TNT under anaerobic conditions has several advantages over aerobically based processes, probably the most important being the cost savings gained by eliminating the need to introduce oxygen. This costly step is often the limiting factor in the aerobic biodegradation of many compounds.

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) appears to be more susceptible to biodegradation under anaerobic than aerobic conditions (Kitts, Cunningham, and Unkefer 1994; McCormick, Cornell, and Kaplan 1981; Walker and Kaplan 1992). The anaerobic biodegradation pathway of RDX in aqueous media involved the sequential formation of hexahydro-1-nitroso-3,5-dinitro-, hexahydro-1,3-dinitroso-5-nitro-, and hexahydro-1,3,5-trinitroso-1,3,5-triazine. Further reduction of the nitro groups resulted in the destabilization and fragmentation of the ring (McCormick,

Cornell, and Kaplan 1981). Funk et al. (1993) also reported the biodegradation of RDX under anaerobic conditions. The biodegradation pathway was not reported although they did conclude that ring cleavage occurred. The biodegradation of RDX in compost (Gorontzy et al. 1994; Kaplan 1992) and by an aerobic microbial consortium (Kaplan 1992) has been reported. More recently, a microbial isolate was described that used RDX as the sole source of nitrogen under aerobic conditions (Binks, Nicklin, and Bruce 1995).

Another nitramine explosive, octahydro-1,3,5,7-trinitro-1,3,5,7-tetrazocine (HMX), also appears to be more susceptible to biodegradation under anaerobic than aerobic conditions (Walker and Kaplan 1992). The formation of mono- and dinitroso intermediates, which were resistant to further biodegradation, was observed. The formation of $^{14}\text{CO}_2$ was observed from radiolabeled HMX during composting experiments although no intermediates were identified (Doyle et al. 1986).

The biodegradation of nitroglycerin (glycerol trinitrate) has been observed under aerobic conditions. Nitroglycerin has been shown to be biodegraded stepwise to glycerol dinitrates and glycerol mononitrates followed by the formation of glycerol (Wendt, Cornell, and Kaplan 1978; Meng et al. 1995), which can be mineralized under aerobic or anaerobic conditions. Nitroglycerin does not appear to serve as a growth substrate (Meng et al. 1995; Pesari and Grasso 1993), although it apparently can serve as a sole source of nitrogen (Meng et al. 1995). A better understanding of the factors controlling the biodegradation of nitroglycerin will help to devise treatment strategies enhancing the transformation rates.

Nitroglycerin wastewaters are often chemically desensitized using calcium hydroxide (Kaplan, Cornell, and Kaplan 1982). This treatment removes glycerol trinitrate, glycerol dinitrate, and glycerol mononitrate, but results in the formation of the epoxides glycidol and glycidyl nitrate. Both of these epoxides abiotically degrade (spontaneously) forming glycerol and glycerol 1-mononitrate, respectively, although the degradation rates can be enhanced by microbial activity. In sterile controls, glycidyl nitrate was abiotically degraded to predominantly glycerol 1-mononitrate; while in batch studies, inoculated with growing microorganisms, the glycerol 1-mononitrate was partially biodegraded (Kaplan, Cornell, and Kaplan 1982; White and Snape 1993).

Kaplan et al. studied the biodegradation of nitroguanidine under aerobic and anaerobic conditions (Kaplan, Cornell, and Kaplan 1982; Walker and Kaplan 1992). They found that nitroguanidine was biodegraded under anaerobic, but not aerobic conditions to a variety of products. The degradation of nitroguanidine to nitrosoguanidine was biologically mediated, while the subsequent formation of

cyanamide, nitrosamide, cyanoguanidine, melamine, and guanidine from nitroso-guanidine were nonbiologically mediated.

Nitrocellulose is generally considered recalcitrant to biodegradation (Walker and Kaplan 1992). It was shown that chemical pretreatment by alkaline hydrolysis was necessary to generate a modified polymer susceptible to microbial degradation. Kaplan suggested that studies concluding nitrocellulose was biodegraded as evidenced by microbial growth may have mistakenly attributed the growth to contaminants in the growth media or to biodegrading regions of nitrocellulose that have an incomplete or low degree of nitrate substitution. Other mechanisms of degradation were not eliminated, such as effects of secondary metabolites on the chain chemistry inducing abiotic degradation of the polymer, giving rise to the formation of metabolites that could be used by the microorganisms for microbial growth (Walker and Kaplan 1982).

Brodman and Devine (1981) reported the growth of *Aspergillus fumigatus* using nitrocellulose (pyroxylin) as the nitrogen source when growing on glucose. The fungus used nitrogen resulting from a hydrolysis reaction liberating nitrate. Actual growth yields were slightly more than expected, suggesting the fungus may have enhanced the hydrolysis reaction rate. Later studies by this laboratory reported a 20 percent loss of the initial nitrocellulose concentration, which was attributed to biodegradation by several other fungal strains (Sharma et al. 1995). Gallo et al. (1994) reported the biodegradation of nitrocellulose in liquid culture by an actinomycete and fungus. The authors observed decreases in the molecular and dry weight of nitrocellulose as evidenced by gel permeation chromatography and gravimetric losses in aqueous media, respectively. In other studies, nitrocellulose was reduced from 13.3 to 10.1 percent nitrogen under methanogenic conditions when methanol was added as a growth substrate (USACERL researcher Dr. Byung Kim, personal communication). Composting has been successfully used to reduce the nitrocellulose concentration of contaminated soils, but the relative contributions of sorption and chemical, physical, and microbiological degradation were not determined (Williams, Ziegenfuss, and Sisk 1992).

Composting

Composting is a biological treatment process that results in the microbial-mediated decomposition of organic matter (Hogan, Miller, and Finstein 1989; Fogarty and Tuovinen 1991). The composting process can be divided into four major microbiologically important phases dictated by the temperature: (1) the mesophilic phase, (2) the thermophilic phase, (3) the cooling phase, and (4) the maturation phase. The composting process begins in the mesophilic temperature

range (20 to 45 °C). As microbial respiration increases during organic matter decomposition, the temperature increases and enters the thermophilic temperature range (>45 °C). The greatest amount of organic matter decomposition and biomass formation occurs in the thermophilic temperature range. As organic matter becomes limiting for microbial respiration, the composting process enters a cooling phase followed by a maturation of the compost. A mature compost is considered stabilized when the available organic matter has been depleted and little remains to support microbial respiration (Fogarty and Tuovinen 1991).

Several parameters need to be controlled to optimize the composting process, including oxygen, moisture, pH, carbon-to-nitrogen ratio, and temperature. Moisture and temperature should be maintained between 40 and 60 percent of water-holding capacities and 25 and 60 °C (77 and 140 °F), respectively. The starting pH of the compost should be near neutral (pH 7) and will typically range between 6 and 8 during the composting process. The beginning carbon-to-nitrogen ratio should range between 26 and 35 (Fogarty and Tuovinen 1991). This is achieved by combining different volumes of compost amendments.

Perhaps the most important parameter controlling the composting process is the availability of oxygen (Fogarty and Tuovinen 1991). Composting is enhanced with adequate levels of oxygen; thus adequate penetration of oxygen into the pile is a necessity. Aeration should ensure oxygen levels within the pile are maintained between 5 and 15 percent, while some studies recommend that oxygen in the circulating air should not fall below 18 percent (Fogarty and Tuovinen 1991). Regardless of the type of aeration system used, it is thought that anaerobic microsites and zones do exist in compost piles (Williams, Ziegenfuss, and Sisk 1992; Fogarty and Tuovinen 1991). The presence of anaerobic zones may help to explain the loss of RDX in compost (Williams, Ziegenfuss, and Sisk 1992) because studies conducted in aqueous media have observed biodegradation under anaerobic conditions only (McCormick, Cornell, and Kaplan 1981).

Composting has gained acceptance in the last two decades as a method of disposal and volume reduction for municipal and agricultural wastes (*The BIOCYCLE Guide* 1989). Composting has also been proposed as an alternative treatment technology to incineration for disposing of explosives-contaminated soils (Griest et al. 1993). Composting is perceived as a desirable alternative to incineration because: (1) it is a biologically based process thought to be less costly than incineration, (2) it converts the energetic compounds to innocuous end-products, and (3) it is perceived by the public as an environmentally friendly technology. Several studies suggest that composting may be used to clean up explosives-contaminated soils. As a result of these studies, the Army used composting for the first time in 1994 to clean up explosives-contaminated soil at a National Priorities

List Site (Duchnowski 1994). Although further studies and demonstrations will be needed before composting explosives-contaminated soils can be used more frequently, the results suggest that composting may be a potential alternative treatment method. The major findings of laboratory and field studies on composting explosives-contaminated soils are discussed below.

Case Studies: Composting Explosives-Contaminated Soils and Propellants

Louisiana Army Ammunition Plant

Laboratory, pilot, and field scale studies have been carried out at the Louisiana Army Ammunition Plant (LAAP) to investigate composting as a treatment method to dispose of lagoon sediments contaminated with 2,4,6-trinitrotoluene (TNT), hexa-hydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-trinitro-1,3,5,7-tetrazo-cine (HMX), and tetryl (Ayorinde and Reynolds 1991; Doyle et al. 1986; Williams, Ziegenfuss, and Marks 1989; Williams, Ziegenfuss, and Sisk 1992).

Laboratory studies demonstrated the transformation of RDX, TNT, and tetryl, although only RDX was mineralized as evidenced by the formation of $^{14}\text{CO}_2$ from radiolabeled parent substrates. Most of the ^{14}C -labeled carbon of TNT and tetryl were found in the organic matter after solvent extractions. RDX was mineralized in the compost amended with sewage sludge, but not hay-horse feed.

Field scale studies were conducted to evaluate the effect of temperature on the composting process. Lagoon sediments contaminated with TNT, RDX, HMX, and tetryl were mixed with horse manure, straw, alfalfa, horse feed, and fertilizer and composted for 153 days. The total explosive concentrations in both the mesophilic and thermophilic composts were decreased from 17,000 mg/kg to less than 400 mg/kg (Williams, Ziegenfuss, and Marks 1988). With the exception of RDX, there was little mineralization of the compounds to CO_2 and H_2O , and loss of the parent compounds and/or biotransformation products was attributed mainly to sorption to organic matter.

Badger Army Ammunition Plant

Laboratory and pilot scale composting studies were conducted with nitrocellulose-contaminated soil obtained from the Badger Army Ammunition Plant (BAAP) (Doyle et al. 1986). Laboratory studies concluded that biodegradation of nitrocellulose was complete after 4 weeks of composting and that 43 to 74 percent of the radiolabeled nitrocellulose was recovered as $^{14}\text{CO}_2$ (Doyle et al. 1986). Field studies on composting nitrocellulose-contaminated soils demonstrated that, after

151 days, there was a 28 percent and >98 percent reduction in nitrocellulose, respectively, in mesophilic and thermophilic-incubated compost piles. Further studies with compost systems under thermophilic conditions demonstrated >99.6 percent reduction in nitrocellulose with soil-loading rates ranging from 22 to 32.5 percent (V/V), although some studies suggested soil-loading rates as high as 60 percent were amenable to biodegradation. The authors concluded that composting was an effective technology for reducing the concentration of nitrocellulose in the contaminated soils. Although the mechanism(s) responsible for depleting nitrocellulose from the compost were not determined, it was presumed to be biodegradation (Williams, Ziegenfuss, and Marks 1989).

Umatilla Depot Activity

A number of composting studies have been conducted at Umatilla Depot Activity (UMDA) (Griest et al. 1992; Williams and Marks 1991). Static pile and mechanically agitated compost approaches were evaluated for treating soil contaminated with TNT (13,000 mg/kg), RDX (1000 mg/kg), and HMX (300 mg/kg). Explosive removal rates ranged from 77 to 99 percent for TNT, zero to 93 percent for RDX, and 2 to 80 percent for HMX, depending on soil-loading rates and variations in compost amendments. The authors concluded that mechanically agitated reactors performed better than static piles, and that biodegradation rates decreased with soil-loading rates greater than 30 percent (Williams and Marks 1991).

Later studies conducted at Umatilla evaluated windrow composting and compost seeding (Hammel et al. 1993). Recycling of acclimated compost into newly formed aerated static piles did not enhance the depletion of the explosives. The authors observed >99 percent and 76 percent reductions in TNT, RDX, and HMX at the end of 40 days in the aerated windrow piles, respectively, while in the unaerated windrows, the reductions were >99 percent for TNT, RDX, and HMX. The authors concluded that windrow composting was more effective than aerated-static-pile and mechanically-agitated-in-vessel composting systems (Williams and Marks 1991).

Several studies have demonstrated the presence of toxicity in compost residue, although it was not determined if it was due to the presence of the explosive compounds (Griest et al. 1990). This finding prompted a study on the toxicity and mutagenicity of residue from the field studies conducted at Umatilla (Griest et al. 1992).

With a 10 percent soil loading, the specific mutagenicity decreased more than 85 percent over a 90-day composting time. TNT or its metabolites accounted for less

than 5 percent of the observed specific mutagenicity; the remaining unaccounted activity was due to either an undetected compound(s) or other unknown compounds formed during composting. There was no observed specific mutagenicity in the control compost pile containing 10 percent noncontaminated soil. The toxicity (EC50) of the compost piles to *Ceriodaphnia dubia* decreased approximately fourteenfold at the end of 90 days. Interestingly, there was some toxicity of the control compost that did not contain explosive material. The toxicity associated with these compost piles decreased by approximately 2.5-fold over the same period; at the end of the experiment, the toxicity in the piles containing the 10 percent contaminated soil was approximately sixfold greater than the control pile. The authors concluded that the remaining toxicity was reduced to levels unlikely to be of human concern (Griest et al. 1993).

Only one study was found that investigated the composting of single base propellants. The propellants, WC860 and H5010, contain approximately 79 and 89 percent nitrocellulose, respectively. The studies were carried out in an in-vessel compost system containing 10 kg dry weight compost amendments and 200 g of the propellant. The authors concluded that 83 and 74 percent of WC860 and H5010, respectively, were depleted in 8 weeks (Brown 1994). It was stated that additional biodegradation would likely have taken place if the physical size of the propellants were reduced to increase the surface area of the propellants. Although significant reductions in nitrocellulose were observed, no end-products or metabolic intermediates were reported, nor were the relative contributions of abiotic and biotic factors responsible for the loss of nitrocellulose determined. However, the results are promising and suggest that composting may possibly be used to treat some types of munition production wastes after further study.

Cost Evaluation of Field Scale Composting

Little information exists regarding the cost of composting energetic compounds. Although the Army has investigated the economics of composting nitrocellulose fines and explosives-contaminated soils, it remains difficult to predict the costs for composting munition production wastes because of unknown variables. Nevertheless, it seems worthwhile to briefly review several studies that highlight the cost savings of composting nitrocellulose fines and explosives-contaminated soils over traditional technology (typically incineration). Although the cost of composting munition production wastes would likely be different, the savings realized would probably be similar to those cited in the following studies.

Composting Nitrocellulose Fines

A cost analysis for composting nitrocellulose fines generated at Radford Army Ammunition Plant was performed using static pile and in-vessel processing systems (Breed et al. 1991). For the static pile analysis, the study estimated costs for treating 2000 and 6000 lb per day of dry nitrocellulose.* The underlying assumptions and operating principles for the two sizes of waste streams were the same, except for the amount of capital equipment and labor required to operate the plants (Breed et al. 1991). Briefly, the major assumptions are:

1. Biodegradation rates similar to those seen in composting nitrocellulose-contaminated soils
2. Reduction of nitrocellulose concentrations to 50 mg/kg after 40 days
3. A beginning nitrocellulose concentration of 5 percent (w/w)
4. An initial carbon:nitrogen ratio of 10:1
5. No additional curing of the compost after the destruction of nitrocellulose.

The capital costs for the smaller and larger systems were \$3.65 and \$7.77 million, respectively. The final operating costs for composting nitrocellulose fines for the smaller and larger facility were estimated to be \$455.00 and \$754.00, respectively, per dry ton nitrocellulose.

The cost analysis for in-vessel composting was estimated for treating 6000 lb per day of a 10 percent nitrocellulose aqueous slurry based on the operating costs provided by three commercial facilities composting sewage sludge and food waste. The capital and operating costs ranged from \$5.8 to \$12.2 million and \$471.00 to \$772.00 per ton of dry nitrocellulose, respectively. These estimates are much less than the \$2000.00 per dry ton estimated for incineration (Breed et al. 1991).

Composting Explosives-Contaminated Soils

A cost analysis was undertaken for composting munition-contaminated soils using a windrow approach. The cost analysis is based on treating 20,000 tons of contaminated soil over a period of 1 to 10 years. The total cost of treating a ton of soil, which includes capital and annual operating costs, are \$366, \$223, \$211, \$216, and \$214 for a treatment period of 1, 3, 5, 8, and 10 years, respectively. Composting was approximately 40 percent less costly than incineration (Lowe et al. 1993). The cost per ton (not including excavation and final disposal) for

* 1 lb = 0.453 kg.

composting and incineration were \$187.00 and \$300.00, respectively, for treating 20,000 tons over a 5-year period.

3 Research Needs and Strategies for Composting Energetic Material Production Wastes

The literature review clearly indicates that some explosives are biodegradable and that, in some cases, soils contaminated with them can be treated by composting. Before discussing specific areas requiring further study, source separation of the energetic material and the experimental approach need to be addressed.

Source separation involves removing from the waste stream material that will not be composted. Energetic material contaminated waste (EMCW) is a mixture of items that include wood, cloth, solvents, bags, boxes, and cans that may or may not be contaminated with energetic material. Although cellulosic-based material may potentially be composted, solvents and cans most likely will not. Waste streams will need to be evaluated case by case with regard to how and what types of compounds will be removed from the waste stream before entering a compost pile. Some of the more dense material, such as wood, may have to be reduced in size before composting, or, alternatively, it may be removed after composting. Regardless of the approach eventually taken, these issues can be dealt with and studied more thoroughly after deciding which munition production wastes, if any, may be disposed of by composting.

Other important issues are the statistical, analytical, and experimental approach taken in composting studies. These issues are important for gathering unbiased and objective scientific evidence from laboratory and field studies. If composting is a useful technology, the supporting evidence should unequivocally support this position by documenting the role of biology in the depletion of the energetic material. This implies that depletion of the energetic material by mechanisms other than biodegradation need to be quantitated. This can be done in the laboratory as well as in the field by using experimental controls that eliminate the role of biology by using inhibitors or sterile compost material. This is important because loss of the energetic material from a compost pile is not synonymous with the material's biodegradation; the composting study needs to document and link the role of biology to the depletion of the energetic material. This experimental

approach should also require that studies be carried out in replication and, when appropriate, the statistical significance of results reported.

One issue remains: how the composting of munition production wastes should be approached. The biodegradation of explosives is complex and involves many factors. However, the factors can be subdivided into three interrelated areas so that, if studied from this perspective, recommendations can be made in a logical and organized way. To this end, the composting or biodegradation of energetic material production wastes should be considered in the context of: (1) the physiology of the microorganisms, (2) the chemistry of the explosive, and (3) the environmental conditions of the surrounding matrix (Suflita 1989a). A strong foundation must be established in these fundamental, interrelated areas so appropriate strategies can be developed to overcome the factors limiting biodegradation of the energetic compounds in compost. The general principles governing these interrelated areas are considered below.

Physiological Barriers to Biodegradation

Microorganisms are the catalysts responsible for destroying energetic compounds in compost or by some other biological treatment system. If the requisite microorganisms are absent, biodegradation will not take place. Composting typically is performed by pooling together different types of waste organic matter, all of which typically contain an abundant and diverse microbial population capable of rapidly acclimating to a diverse array of substrates that are used for growth. If the requisite microorganisms for biodegrading the munition production waste are absent, it is unlikely that, under normal circumstances, they will be found elsewhere by using a different source of compost amendment, so approaches other than compost amendment should be pursued.

Even if the requisite microorganisms are present, the energetic compound(s) will not be biodegraded if other compounds are present that inhibit the microorganisms or if the energetic compounds are present at concentrations high enough to inhibit micro-organism growth. Relatively little is known about the toxicity of some energetic compounds (Drzyzga et al. 1995), the effect of composting on explosives (Griest et al. 1993), or of the additives that are typically added to propellant formulations. Propellants are a mixture of compounds containing, in addition to the energetic compound(s): ballistic modifiers, stabilizers, and gelatinizing agents, which may or may not be toxic and/or inhibitory to the microorganisms.

Some compounds have a threshold concentration below which biodegradation does not occur (Suflita 1989a; 1989b); such a threshold may exist for energetic

compounds as well. If a threshold concentration exists and is above the regulatory or target concentration, composting may not be satisfactory. Threshold concentrations must be established for munition production wastes in the laboratory and compared with known regulatory limits.

If the requisite microorganisms are present and the munition production wastes are not inhibitory, the target compound will still be metabolized poorly if it cannot enter the microbial cells (Suflita 1989a). Energetic compounds are relatively water insoluble, a characteristic that makes it difficult for microorganisms to transport the compounds intracellularly. In studies on composting explosives-contaminated soils, the energetic compounds were distributed relatively uniformly throughout the soil, maximizing the contact between the explosives and microorganisms. Munition production wastes have a relatively low surface-area-to-volume ratio, which decreases the availability of the energetic compounds to the microorganisms even more. Thus increasing the surface area and the availability of the munition production wastes to the microorganisms is of prime importance. Size reduction (increasing the surface area) is of concern for physical and chemical treatment processes as well. Size reduction by hydromilling is being addressed in other Army research efforts. Other pretreatment steps, such as alkaline hydrolysis of nitrocellulose, have been suggested before final disposal using biological processes (Wendt, Cornell, and Kaplan 1978).

An additional factor limiting the water solubility of the energetic compound and thus the ability of the microorganisms to transport them intracellularly is the inclusion of plasticizers, stabilizers, and waxes in propellant formulations (Yinon and Zitrin 1993). The plasticizers and waxes impart rigidity and hydrophobic properties to the propellants, making them even more resistant to biodegradation by limiting the solubility and dissolution rate of the individual components into the aqueous phase where it is available to the microorganisms. However, the availability of the substrates can be enhanced by appropriate pretreatment steps (as discussed above).

Interestingly, a physical manifestation of the composting process may enhance the availability of munition production wastes to biological activity. When temperatures in the moderately thermophilic range (40 to 60 °C) are characteristically reached (Fogarty and Tuovinen 1991), not only does the solubility of substrates increase with increasing temperatures, but the abiotic degradation of nitrocellulose and physical deterioration of propellants is accelerated (Perrault et al. 1979). Physical deterioration of propellants would likely increase the exposure and thus the availability of all the constituents in the propellant formulation to microbial activity. Thermal degradation of nitrocellulose would also likely enhance its susceptibility to further biodegradation. Studies evaluating the effects of

temperature on the physical properties of propellants and the subsequent effect on their biodegradation may provide strategies for enhancing their biodegradation.

Other biological treatment processes specifically using thermophilic (heat-tolerant) microorganisms, thus providing a dual biological-physical treatment process, may be potential strategies to try. For example, some thermophiles can grow at temperatures greater than 100 °C while degrading cellulose, a polymer similar to nitrocellulose.

Other extremophilic microorganisms, such as acidophiles and alkaliphiles, are capable of growing in (respectively) very acidic or alkaline conditions (Lowe, Jain, and Zeikus 1993), conditions under which nitrocellulose is hydrolyzed (Urbanski 1965). Developing dual biological-chemical or physical treatment processes may offer some potential strategies that work together synergistically to degrade the propellants. This may be carried out in various configurations such as in an aqueous or solid-phase environment. Another possibility is to use microorganisms to produce extracellular enzymes that act on the energetic material, precluding the need for the compounds to be transported intracellularly. Some fungi, for example, by producing nonspecific extracellular enzymes, can biodegrade energetic compounds (Barr and Aust 1994).

Chemical Barriers to Biodegradation

A very important factor in a compound's susceptibility to biodegradation is its chemical structure. The more similar a contaminant is to naturally occurring organic compounds, the easier it will be to enter into main metabolic pathways to be metabolized (White and Snape 1993). There are no naturally occurring nitrate-ester compounds so many of the energetic compounds containing nitrate ester functional groups are foreign to microorganisms (are xenobiotic). Host microorganisms therefore have not developed the ability to biodegrade these compounds. For example, although microorganisms can biodegrade nitroglycerin, it does not appear to be used as a growth substrate (Meng et al. 1995).

Another important factor is the length of time the microorganisms have been exposed to the particular contaminant. Microorganisms can develop the capability to biodegrade what were once considered recalcitrant compounds. This is why the source of inoculum may be important in developing biological treatment systems to dispose of energetic compounds. Compounds that appear to be recalcitrant to microbial degradation may be biodegraded with a microbial inoculum from a site that has a long-term history of explosives contamination. It is more likely that

microorganisms in chronically contaminated sites will have been naturally selected for and/or acclimated to the energetic compound(s).

Although research is beginning to explain the biodegradation pathways for some of the explosives, such as TNT, RDX, nitroglycerin, and DNT (e.g., see introduction above), a better understanding of the responsible microorganisms and the factors controlling their biodegradation are needed. Even less is known about the biodegradation of HMX, nitrocellulose, ammonium perchlorate, polyurethane, polybutadiene, and phosphorus. The effect of secondary substrates such as waxes, ballistic modifiers, stabilizers, and gelatinizers on the biodegradation of the explosives is also not well understood. This requires further research with a variety of propellants, such as Comp B and other single-, double-, and triple-base propellants.

Environmental Barriers to Biodegradation

Microorganisms survive under a range of environmental conditions. Extremes of pH, salinity, and temperature can often inhibit a micro-organism's metabolic activity (Suflita 1989a). The microorganisms' metabolic activities are also influenced by the predominant flow of carbon and energy in the system, which is determined by the electron acceptors available to the microorganisms. Environmentally important electron acceptors include oxygen, nitrate, ferric iron, sulfate, and carbon dioxide. If the environment is a well aerated matrix, oxygen will be the preferred electron acceptor.

However, if oxygen is absent, other electron acceptors will be used. These anaerobic microorganisms often have different metabolic capabilities from their aerobic counterparts. How energetic compounds are metabolized and the types of microorganisms metabolizing them under anaerobic conditions is not well understood. Having an understanding of the conditions conducive to the biodegradation of a specific energetic compound allows treatment strategies to be developed. For example, RDX and HMX are more readily biodegraded under anaerobic than aerobic conditions (McCormick, Cornell, and Kaplan 1981; Walker and Kaplan, 1992). Attempting to treat these compounds by composting (which is an aerobically based treatment operation) may not be the preferred method. A better strategy to enhance their biodegradation may be to allow the compost pile to become depleted of oxygen, a condition not usually allowed to develop during composting because the process slows the biodegradation of the naturally occurring organic material and compost amendments. After RDX and HMX are biodegraded under anaerobic conditions, the compost pile is returned to its normally preferred aerobic state to maximize the biodegradation of the remaining energetic

compounds and organic matter. Understanding the environmental conditions needed for the biodegradation of energetic material production wastes may lead to other similar treatment strategies to enhance their biodegradation.

4 Summary

The literature clearly demonstrates that many explosives are biodegradable and that some explosives-contaminated soils can also be treated by composting. A potential does exist to treat munition production wastes by composting or by other biological treatment processes. However, further investigation is needed before this technology can be applied in the field, including:

1. Research to determine what energetic compounds can be biodegraded
2. Research to determine the conditions under which biological treatment processes can occur
3. An evaluation of the biodegradation of energetic compounds in propellant formulations to ensure that other compounds are not inhibitory or toxic to the microorganisms used in the treatment
4. Pilot scale testing in the field.

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Abbreviations

AAP	Army Ammunition Plant
AMC	Army Materiel Command
ARS	Arsenal
BAAP	Badger Army Ammunition Plant
DNT	Dinitrotoluene
EM	Energetic material (waste)
EMCW	Solid waste contaminated with energetic material
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
LAP	Load, assemble, and pack
OB	Open burning
OD	Open detonation
RAAP	Radford Army Ammunition Plant
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
TNT	Trinitrotoluene
UMDA	Umatilla Depot Activity
USACERL	U.S. Army Construction Engineering Laboratories

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